

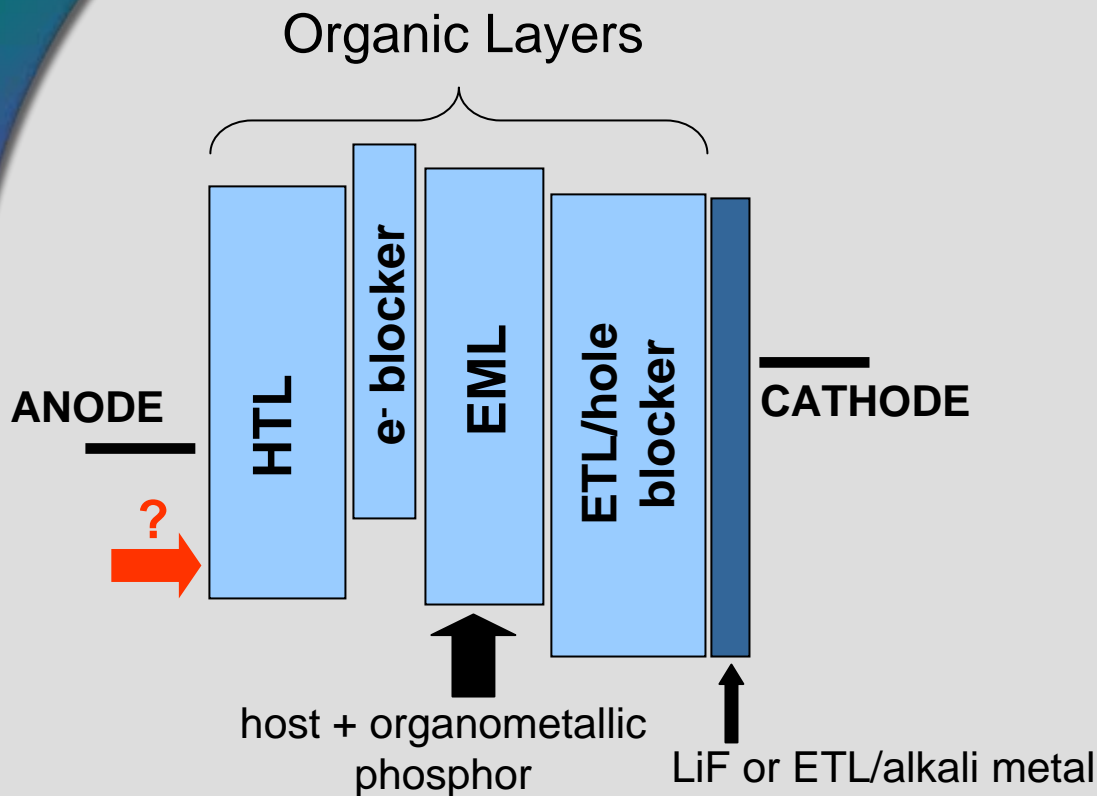
# **High Stability Organic Molecular Dopants for Maximum Power Efficiency OLEDs**

*New Project : Start Date August 2007*

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Presented 01/30/08  
2008 DOE SOLID-STATE LIGHTING R&D WORKSHOP

# Limitations to SSL Power Efficiency Goals for OLEDs



- Energy matching at electrode interfaces lower energy barriers
- Thin layers decrease  $V_{op}$  but pose manufacturing challenges.

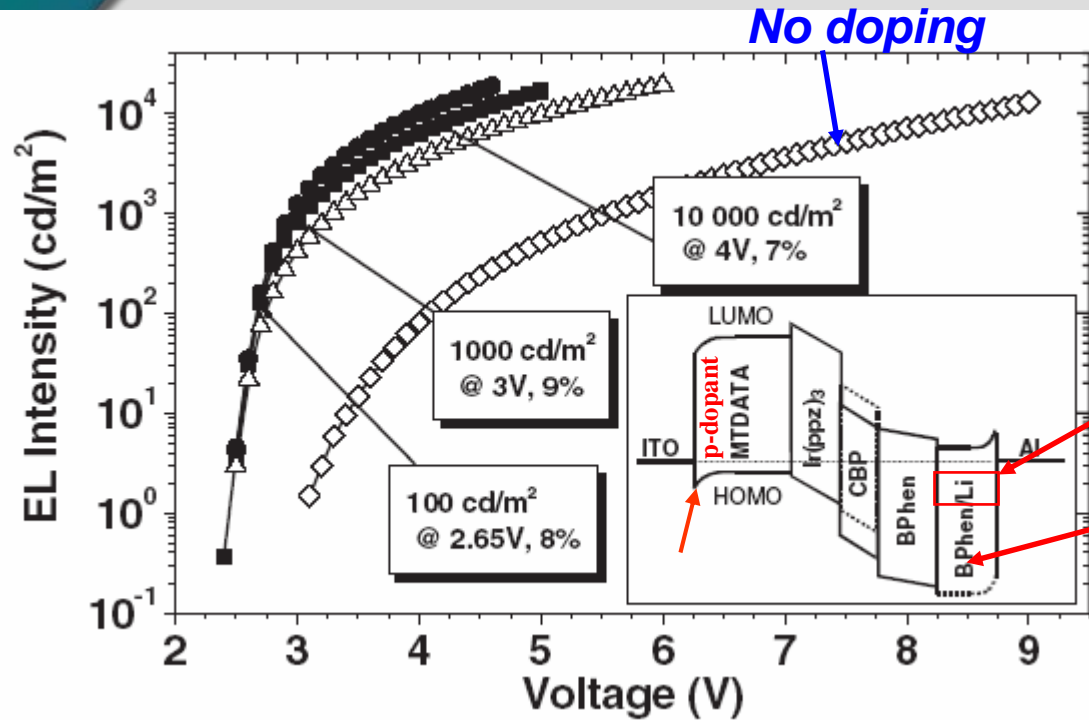
Achieving SSL target power efficiencies in OLEDs requires:

- Near 100% internal QE
  - ✓ electrophosphorescence
  - ✓ charge confining layers

## ALSO NEED:

- Operating voltages close to the bandgap voltage
  - conductivity/electrical doping

# How does conductivity doping work?



## Conductivity doping –

1. *Increases charge injection at organic/inorganic interfaces.* No need to match work function of electrodes with organic layers.
2. *Increases conductivity in bulk layers.* Can use thicker layers without increase in voltage—more practical to eliminate problems with very thin layers (e.g., dust).

Pfeiffer, et al, *Adv. Mater.* **2002**, 14,1633.

Molecular or ionic dopants are believed to work by:

- creating a depletion layer (or accumulation layer) at the organic/inorganic interface (concentrating applied electric field across the interface facilitating charge injection).
- increasing the background charge carrier density in the bulk of the organic thin film (decreasing its series resistance).

# Conductivity Dopants

## Common Reductants (*n*-dopant)

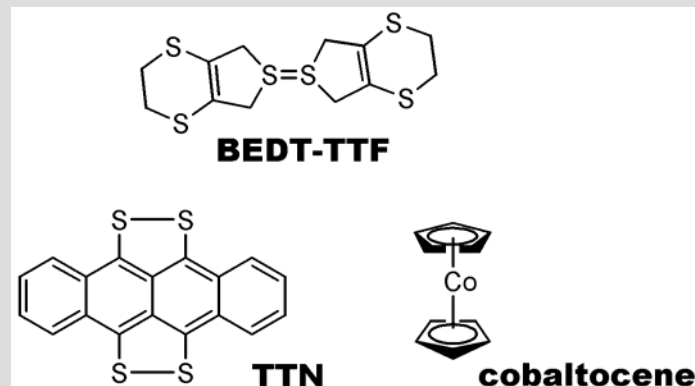
- Li, Na, K, **Cs** (also, LiF, NaF, CsF, etc) – very reactive and *mobile* in organic layers. Reacts to form new materials, new mid gap states detected.

## Common Oxidants (*p*-dopant)

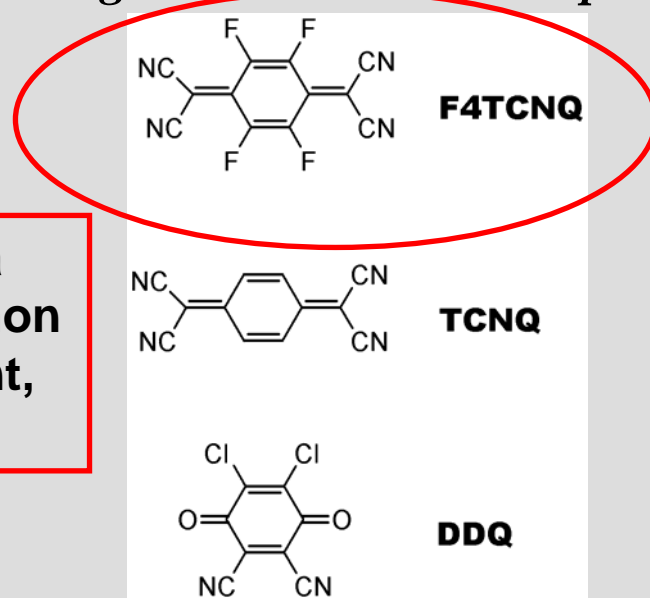
- I<sub>2</sub>, Br<sub>2</sub> – too volatile
- FeCl<sub>3</sub> – coevaporated with HTL, stability poor because of *mobile* ions? Or other?
- SbCl<sub>5</sub> – liquid, only used for solution processing. Stability an issue.

*Very few candidates because of air stability problems.*

## Organic Molecular Donors

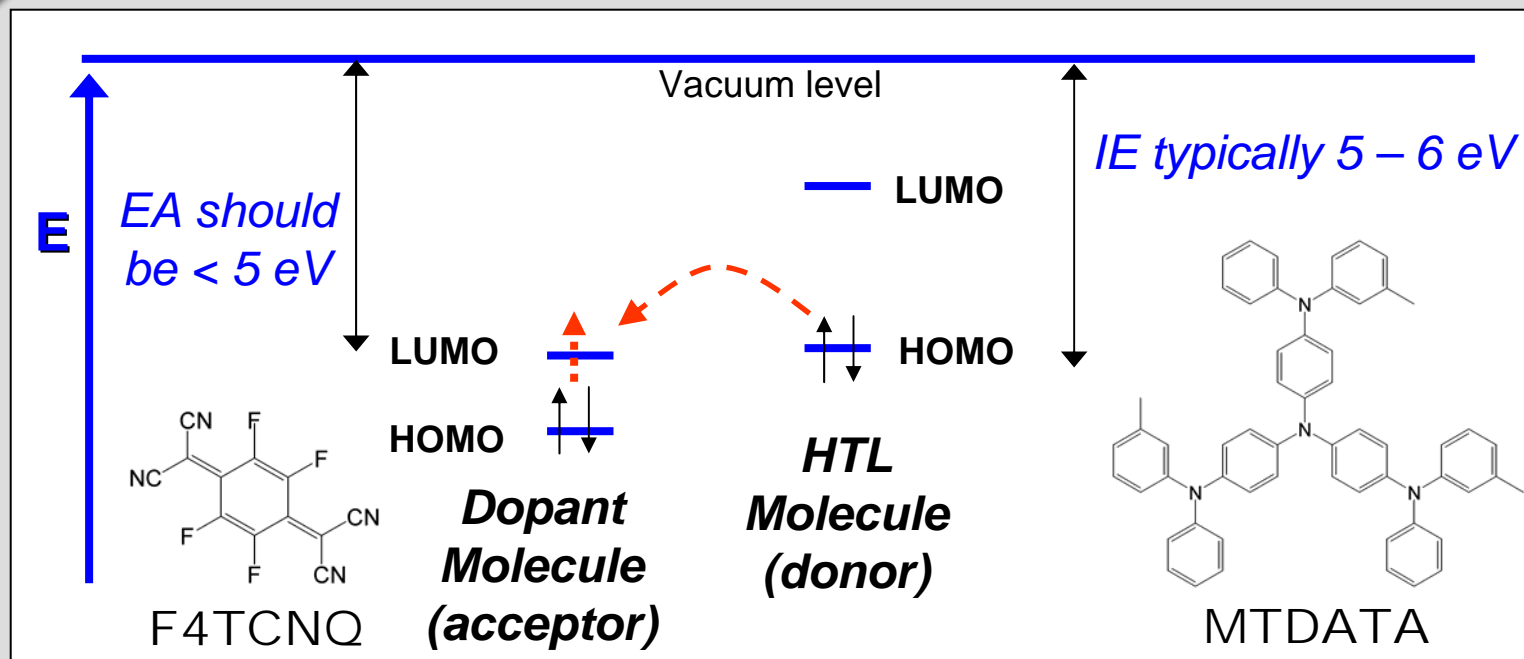


## Organic Molecular Acceptors



**Now a common dopant, but....**

# F4TCNQ – Molecular p-Dopant



## Advantages

- $E_{\text{LUMO}} = 5.2 \text{ eV}$
- High EA
- Stable to sublimation
- Commercially available

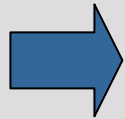
## → Disadvantages

- Limited choice of donors
- Reactive & difficult to purify
- High volatility
- Poor sticking coefficient

## → Problem

- Requires extra layers
- Requires special handling
- Control of dopant amount & diffusion
- Requires buffer layer
- Vacuum system contamination

**NEED:** Molecular acceptor which has high electron affinity, low molecular mobility, good sticking coefficient and lower volatility.



## ANCHORED MOLECULAR DOPANT

**Molecular  
Acceptor**

*Connecting Unit*

**Molecular  
Anchor**

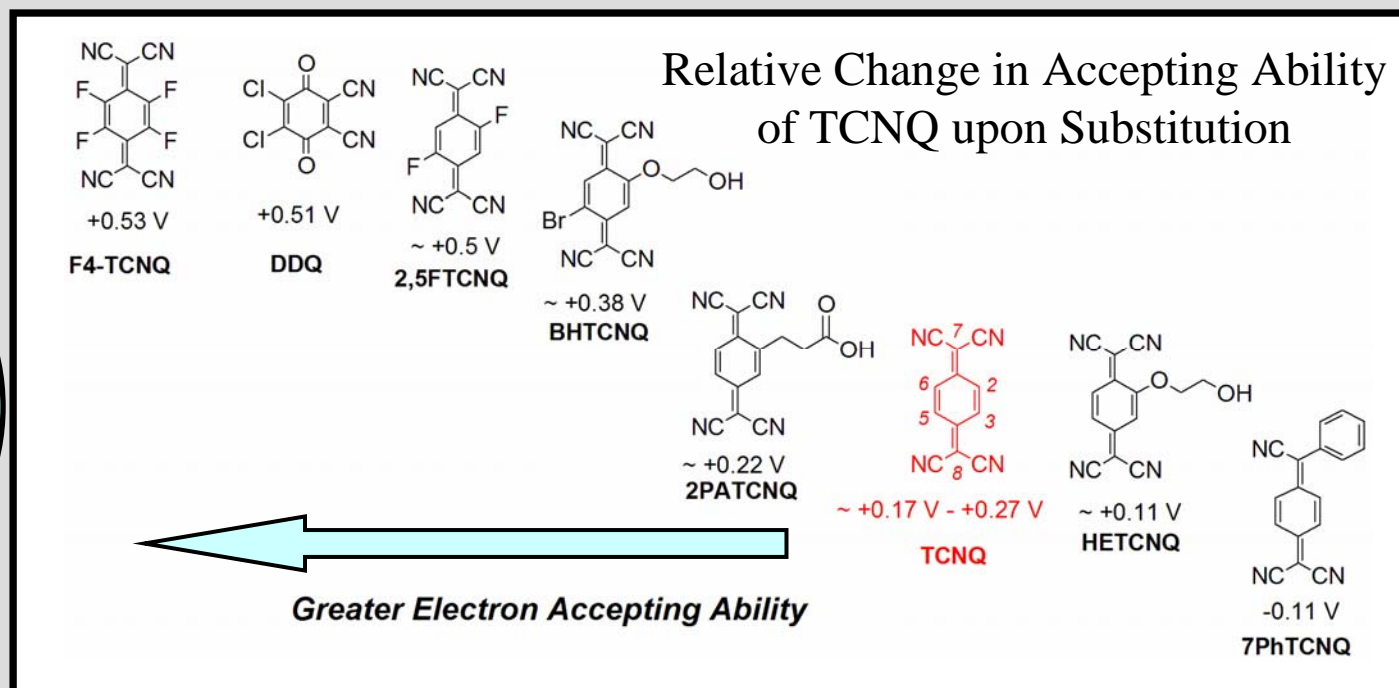
Derivatize  
without  
sacrificing high  
electron affinity

Vary length & rigidity

- 1) Inert to charge transfer reactions
- 2) Rigid, to provide stability in the solid state.
- 3) Multifunctional, to incorporate multiple acceptor sites.

# Molecular Acceptor Design

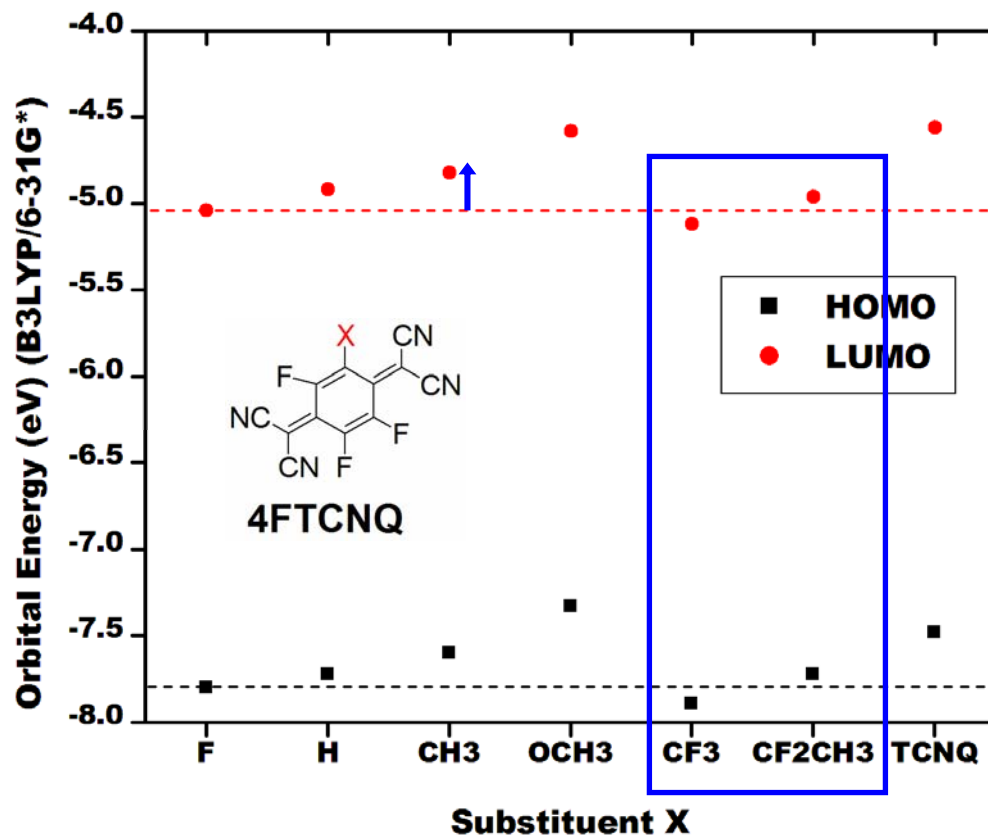
Derivatize  
without  
sacrificing high  
electron affinity



How do the electrochemical properties (i.e.  $E^{\circ}_{red}$ ) change as a function of derivatization?

- EDG-substitution (-OR) and substitution of the dicyanomethine group increases  $E^{\circ}_{red}$ .
- Alkyl-substitution  $\rightarrow$  small effect on  $E^{\circ}_{red}$
- Halogen substitution offsets some of the effects of an EDG.
- Difluorination vs. tetrafluorination of TCNQ report similar  $E^{\circ}_{red}$

# Connecting Unit Design – by Computational Modeling

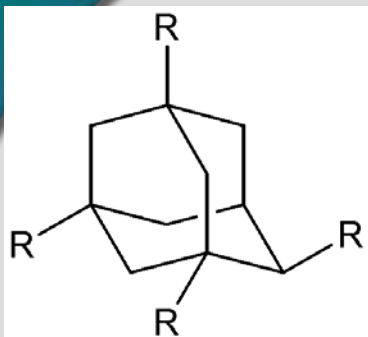


Trends in reduction potentials can be correlated with trends in lowest unoccupied molecular orbital (LUMO) energies for a family of molecules. We use this as a guide to identify candidates for the connecting unit.

-CH<sub>2</sub>- unit can be used, but -CF<sub>2</sub>- would give more effective molecular acceptor.

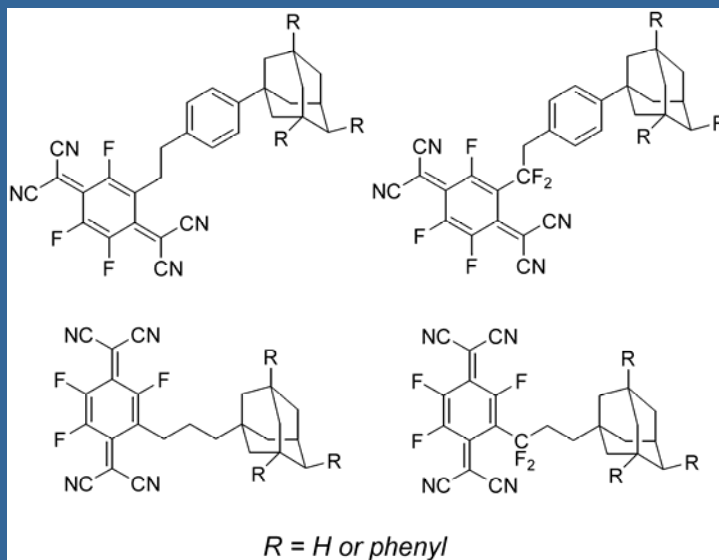


# What about the molecular anchor?



## ADAMANTANE

- 1) Inert to charge transfer reactions
- 2) Rigid, to provide stability in the solid state.
- 3) Multifunctional, to incorporate multiple acceptor sites.



**Target  
Molecule(s)**

**Molecular  
Acceptor**

***Connecting Unit***

**Molecular  
Anchor**

# Project Objectives

**Overall Objective:** To achieve high stability OLEDs with maximum power efficiencies using conductivity doping of charge transport layers.

*We propose to achieve this objective by the development of new organic anchored molecular dopants.*

***Phase I Objective:*** MATERIAL DESIGN & SYNTHETIC METHODOLOGY

***Phase II Objective:*** MATERIAL CHARACTERIZATION AND OPTIMIZATION

***Phase III Objective:*** DEVICE FABRICATION AND OPTIMIZATION

## Year 1 – Proposed Milestones

- Synthesize, purify and characterize 4 anchored-molecular dopants  
Demonstrate stability to vacuum sublimation.
- Electrochemical characterization of all new anchored molecular dopants and demonstration of reduction potentials similar to F4TCNQ.
- Demonstrate p-doping of hole transport layer using one anchored molecular dopant in standard Alq<sub>3</sub> device. Achieve an operating voltage < 5 V for 100 cd/m<sup>2</sup>.

# Project Team

## ▶ **Linda Sapochak, Project Manager**

- Staff Scientist (level V), Ph.D., Chemistry. Material design and characterization.

## ▶ **Paul Burrows**

- Laboratory Fellow (level VI), Ph.D., Physics. Device fabrication and characterization.

## ▶ **Glen Fryxell**

- Staff Scientist (level V), Ph.D., Chemistry. Synthetic methodology development

## ▶ **Asanga Padmaperuma**

- Senior Research Scientist (level III), Ph.D., Chemistry. Synthesis, characterization (structural and photophysical) and computational modeling.

## ▶ **Jonathan Male**

- Senior Research Scientist II (level IV), Ph.D., Chemistry. Materials characterization.

## ▶ **Two postdocs**

- Phillip Koech - Ph.D., University of Texas at Austin, synthetic organic chemistry.
- Xiuyu (Harry) Cai, Ph.D., University of Minnesota, materials science & engineering

# Expected Benefits

Anchored molecular dopants will provide “controlled” conductivity doping of charge transport layers in OLEDs.

- ✓ Lower operating voltage & higher power efficiency
- ✓ Lower manufacturing cost - no separate evaporation chamber
- ✓ Simpler OLED structure – no buffer layer required to prevent dopant diffusion
- ✓ Similar approach may also be applied to new n-dopants.

*The outcome will be lower cost and stable white phosphorescent OLEDs which operate near 100% internal quantum efficiency at close to the bandgap voltage, which in concert with improvements in optical outcoupling will give power efficiencies well in excess of 100 lm/W.*

